

Japanese Unexamined (*Kokai*) Patent Publication No. H4-327582, published November 17, 1992; Application No. H3-94391, filed April 24, 1991; Inventors: Isao FUKUDA, Eiji KOGA, Takehisa NAKANISHI; Assignee: Mitsui Toatsu Kagaku KK

MANUFACTURING METHOD OF EPICHLOROHYDRIN

[Claim]

[Claim 1]

Manufacturing method of epichlorohydrin, characterized in that, with a method of manufacturing epichlorohydrin in the presence of a catalyst from allyl chloride and alkyl hydroperoxide, after the concentration of 1,5-hexadiene contained in the allyl chloride is reduced to 0.1% by weight or less, it is used in a reaction.

[Detailed Explanation of the Invention]

[0001]

[Field of Use in Industry]

The present invention concerns a manufacturing method of epichlorohydrin.

[0002]

[Prior Art Technology]

Regarding methods for reacting allyl chloride and alkyl hydroperoxide in the presence of a catalyst of a compound of molybdenum, tungsten, titanium, tantalum, niobium, vanadium, zirconium, or boron, and synthesizing epichlorohydrin, for methods using a uniform catalyst, those of Japanese Examined Patent Publication Nos. S48-19609 [published in 1973] and S45-17649 [published in 1970] are known, and for methods using a non-uniform catalyst, West German Patent No. 2334315; U.S. Patent No.

4021454; *Journal of Catalysis*, v. 31, n. 438 (1973); Japanese Unexamined Patent Publication No. S52-7908 [published in 1977]; Japanese Examined Patent Publication No. S54-40526 [published in 1979]; Japanese Unexamined Patent Publication No. S64-257701 [published in 1989] disclosed by the present inventors; and the like, are known. [0003]

Regarding a representative operation of recovering epichlorohydrin from a reactive mixture obtained from these methods, first, excess allyl chloride is removed by distillation; then, after the epichlorohydrin in the remaining liquid is recovered, the alcohol which is a reduction product of additionally used alkyl hydroperoxide, the alcohol which is the reduction product of the alkyl hydroperoxide used from heavy articles, and epichlorohydrin are separated and recovered. The allyl chloride that is distilled away is resupplied to the reactor vessel, and the alcohol which is the reduction product of the used alkyl hydroperoxide is recovered in an unmodified state, or is converted to alkyl hydroperoxide through a hydrogen addition reaction and an oxidation reaction after being changed to an olefin by a dehydration condensation reaction, and is resued in a reaction with allyl chloride.

[0004]

For the separation and recovery of the epichlorohydrin, a distillation operation is normally used, but commercial epichlorohydrin requires a product of high purity, and the removal of impurities is essential. The admixture of olefin-based compounds in particular significantly reduces the product value of epicholorhydrin. Because the physical properties of some types of olefin-based compounds resemble those of epichlorohydrin, they cannot be removed with a normal distillation operation. Regarding

a method for selectively removing olefin-based compounds from the epichlorohydrin, a method whereby an olefin-based compound undergoes hydrogen addition processing in the presence of a vanadium catalyst is disclosed in Japanese Examined Patent Publication No. S63-46752 [published in 1988].

[0005]

[Problems the Invention is Meant to Resolve]

However, with this method, an expensive catalyst is necessary; also, because a hydride of an olefin-based compound is formed, or because epichlorohydrin is changed to an alcohol and by-products are newly formed due to the fact that a hydrogen addition reaction is executed with a minute amount of the olefin-based compound in the epichlorohydrin, additional distillation equipment is necessary to remove this.

[0006]

[Means for Resolving Problems]

As a result of diligent research to resolve the aforementioned problems, the present invention have arrived at the completion of the present invention. That is to say, the present invention is a manufacturing method of epichlorohydrin, characterized in that, with a method of manufacturing epichlorohydrin in the presence of a catalyst from allyl chloride and alkyl hydroperoxide, after the concentration of 1,5-hexadiene contained in the allyl chloride is reduced to 0.1% by weight or less, it is used in a reaction.

[0007]

With the present invention, because allyl chloride and alkyl hydroperoxide are reacted in the presence of a catalyst and the concentration of 1,5-hexadiene contained in

the allyl chloride is reduced to 0.1% by weight or less, a high-purity epichlorohydrin may be manufactured using a normal distillation operation.

[0008]

The allyl chloride referred to in the present invention is formed by hot chlorination or oxychlorination, and for the main impurities, normally, 0.3 – 0.5% by weight of 1,5-hexadiene and 0.3 – 0.5% by weight of 1-chloropropane are contained. Among these, there is almost no change of the 1-chloropropane to another substance based on a reaction with alkyl hydroperoxide, and this can be easily separated from epichlorohydrin. However, the 1,5-hexadiene epoxidizes from the reaction with the alkyl hydroperoxide, and easily changes to a 1,2-epoxy -5-hexene that is extremely difficult to separate.

[0009]

In the present invention, before the 1,5-hexadiene is used in a reaction from alkyl chloride, it is carefully separated by a distillation operation. There is no limitation in particular with respect to the distillation device and operational method, if there are a distillation tower and operational conditions having a number of theoretical plates wherein 1,5-hexadiene can be separated, this can be carried out with a batch method or a continuous method. However, if the pressure in a reduced-pressure distillation becomes too low, a large quantity of energy becomes necessary for the alkyl choride and light compression cooling, and this is not economical. It is most desirable for no 1,5-hexadiene to be essentially present in the distilled and refined alkyl chloride, but it may be 1,000 ppm per less, or more preferably, 500 ppm or less.

[0010]

The alkyl hydroperoxide is a cumene hydroperoxide, ethyl benzene hydroperoxide, tertiary butyl hydroperoxide, or cyclohexyl hydroperoxide, and may be diluted as necessary in a solvent. Regarding the solvent used for dilution, an item contained as a non-reactive raw material when the alkyl hydroperoxide is manufactured such as cumene or ethyl benzene; an item formed from alkyl hydroperoxide such as dimethyl phenyl carbinol, phenyl carbinol, tertiary butyl alcohol, or the like; and a chlorine-based organic compound such as chlorobenzene or the like may be used.

[0011]

With the present invention, for the mol ratio of the allyl chloride and alkyl hydroperoxide, it is preferable for the allyl chloride to be present in excess; normally, this is 1.1 – 50 mols, more preferably 2 – 20 mols, per 1 mol of alkyl hydroperoxide. At less than 1 mol, a sufficient epichlorohydrin yield rate cannot be obtained, and at greater than 50 mols, a large quantity of energy is consumed for recycling, and this is not economical.

[0012]

The catalyst used in the present invention is an acetyl acetate, alcoholate, naphthonate, chloride, oxide, or carbonyl compound of molybendum, tungsten, titanium, tantalum, niobium, vanadium, or boron. It may be a compound that dissolves in the raw material solution, or an insoluble compound. Also, it may be used in a form where it is affixed to a solid supporting body such as silica gel, alumina, zirconia, or the like. Two or more of these catalysts may be used together. Additionally, in addition to the catalyst, basic substances such as n-butylamine, triethylamine, magnesium oxide, or the like may be caused to be present in the reactive liquid. There is no particular limitation regarding the quantity of catalyst used, but there is 0.01 – 2 mol%, more preferably 0.01 – 1 mol%

of metal in the catalyst for the alkyl hydroperoxide being used. At less than 0.01 mols, a sufficient epichlorohydrin yield rate cannot be obtained, and at greater than 2 mols, it is not economical. The reaction may be carried out either as a batch reaction, or a continuous reaction of a circulation system. The reaction temperature is 0 – 150°C, preferably 20 – 120°C. At lower than 0°C, the reaction is slow, and at higher than 120°C, the dissolution of the alkyl peroxide becomes preferential.

[0013]

The present invention is specifically explained below by means of embodiments.

[0014]

Embodiment 1

(Refinement of allyl chloride)

Using a Helifac filler tower-type batch distillation device, in the conditions of normal pressure, 46°C, and reflux ratio of 10, allyl chloride was distilled, and allyl chloride of the composition shown in Table 1 was obtained.

[0015]

[Table 1]

Component	Before refinement (% by weight)	After refinement (% by weight)
1,5-hexadiene	0.400	0.005
1-chloropropane	0.442	0.440
allyl chloride	99.108	99.509
other	0.050	0.046

(Manufacture of catalyst)

120 ml of anhydrous ethanol and 2.38 g of titanium tetrachloride were added into a flask with an agitator under a nitrogen gas seal and were agitated for 30 minutes. Then, after 60 g of a silica gel were added and this was agitated for 60 minutes, the ethanol was

distilled out under normal pressure, and after being dried at 100°C under reduced pressure, this was baked for two hours at 200°C in an air current. The item, wherein the titanium was affixed to the silica gel, was fed under a nitrogen seal along with 7.4 g of 1,1,1,1-3,3,3-hexamethyldisilazane in an autoclave with an agitator and was heated at 4 hours at 200°C, and a catalyst was obtained.

[0016]

Next, 17 g of the aforementioned catalyst and 17 g of magnesium oxide were filled while mixing in a pressure-resistant glass reaction tube, having a heating jacket, with an inner diameter of 20 mm and a length of 300 mm, and the allyl hydroperoxide obtained from Embodiment 1 and 44% by weight of a cumene solution of cumene hydroperoxide were circulated continuously from the bottom of the reaction tube every hour at a weight ratio of 20 to 8. At this time, the temperature of the heating jacket is adjusted so as to maintain the temeprature of the filler layer at 90°C. After 64 hours, the reactive mixture was analyzed with a glass chromatograph, and the composition was that shown in table 2.

[0017]

[Table 2]

Component	Concentration
Epichlorohydrin	6.22% by weight
Dimethyl phenyl carbinol	12.01% by weight
Cumene hydroperoxide	0.78% by weight
Cumene	14.41% by weight
1,2-epoxy-5-hexene	10 ppm or less
Allyl chloride, etc.	66.60% by weight

After the allyl chloride was distilled off from the reactive mixture, the remaining liquid was precisely distilled under the conditions of a temeprature of 60°C, a pressure of

100 Torr, and a reflux ratio of 10, and the epichlorohydrin was recovered. When the recovered item was analyzed with a glass chromatograph, 1,2-epoxy-5-hexene was not detected.

[0018]

Embodiment 2

1,5-hexadiene was added to the allyl choride after refinement of Embodiment 1, and allyl chloroide comprised of the composition of Table 3 was obtained.

[0019]

[Table 3]

Component	Concentration
1,5-hexadiene	0.035% by weight
1-chloropropan	0.440% by weight
Allyl chloride	99.479% by weight
Other	0.046% by weight

Using this allyl chloride, a reaction was carried out using the same catalyst and reaction device as in Embodiment 2 [sic], and when the epichlorohydrin was distilled and recovered, 0.07% by weight of 1,2-epoxy-5-hexene was present.

[0020]

Comparative Example 1

The allyl chloride before refinement of Embodiment 1 was used, and a reaction was carried out using the same catalyst and reaction device as in Embodiment 2. After 40 minutes, when the reactive substance was analyzed using a glass chromatograph, the composition shown in Table 4 was obtained.

[0021]

[Table 4]

Component	Concentration
Epichlorohydrin	6.25% by weight
Dimethyl phenyl carbinol	12.18% by weight
Cumene hydroperoxide	0.73% by weight
Cumene	14.48% by weight
1,2-epoxy-5-hexene	0.09% by weight
Allyl chloride, etc.	66.27% by weight

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